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DEVICE FOR FIELD DETERMINATION OF HEAVY METALS IN NATURAL WATERS

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F I N A L R E P O R T

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ABSTRACT

DEVICE FOR FIELD DETERMINATION OF HEAVY METALS IN NATURAL WATERS

The objective of this project was the development and testing of a simple, portable, self-contained device suitable for in situ analysis of natural waters for certain trace metals. The trace metals which were of primary interest were copper, lead, cadmium, nickel, chromium and zinc.

Two models of the analyzer were built during the course of this experiment. The first model utilized a rotating platinum electrode in sulfosalicylic acid electrolyte. This was abandoned due to the inconsistent quality of high sensitivity results in the field and the interference of the sulfosalicylic acid medium with analysis of lead and iron ions. The second model used a dropping mercury e l ectrode in the same electrolytic medium. The medium was discarded due to the interference with lead and iron, but the DME was retained with tri-sodium citrate as the medium since this allows analysis of lead, cadmium, zinc and iron.

Details of the construction and field operation of the kit are explained in full. Field sampling techniques are also discussed.

The operation of the device is relatively simple and the cost of construction of the initial model was less than $400. The design of the instrument allows the possibility of future development and adaptations. At present, however, the determination of metals is limited to only four ions. The use of mercury makes careful disposal of waste materials necessary. The results have not been compared with the results from known different tests with known reliability.

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FINAL REPORT

Device for Field Determination of Heavy Metals in Natural Waters - U of I (A-032-ILL)

September 30, 1970

submitted by

Dr. Robert E. Van Atta, Principal Investigator

OBJECTIVES

The objectives of this project were originally stated as the development and testing of a simple, portable, self-contained device suitable for *in situ* analysis of natural waters for certain trace metals. The metals of prime concern (primarily those which are or may be toxic to fish) were copper, lead, cadmium, nickel, chromium, and zinc. It was also anticipated that the simultaneous determination of dissolved oxygen might prove to be feasible.

The subsequent sections of this report describe the extent to which the previously stated objectives have been attained. The development of the instrument and necessary accessories is described and the operational procedure for the device is detailed; typical analytical results obtained with the instrument are presented. A discussion of the advantages, disadvantages, and suggested further development of the device and/or techniques associated with its use conclude the report.

INSTRUMENT DEVELOPMENT

Introduction.--After a considerable amount of trial-and-error experimentation early in the life of the project, a prototype model of the eventual device was constructed and field tested, as previously described in the first and second annual reports for the project. The prototype was designed and constructed along the general lines of the original proposal, i.e., a simple direct current polarographic circuit employing fixed resistors and a multiple position switch. This basic design was soon modified to the application of operational amplifiers permitting employment of the 3-electrode polarographic technique, so that polarographic cell iR drop could be adequately compensated to permit acceptably accurate two-point measurement of wave heights. Several other relatively minor modifications mentioned in earlier reports were also incorporated in both the prototype Model I and the improved Model II described subsequently in this report.

The electrode-electrolyte system employed in a heavy metal analysis by the polarographic method is nearly as important as the fundamental circuit itself and, in fact, controls in some measure, the nature of that circuit. Although a rotating platinum working electrode system was originally proposed for convenience in field operations, that system was found to be impractical and was replaced by the more conventional, though more versatile and potentially more troublesome dropping mercury electrode. Some physical problems were actually encountered in the design of the latter electrode system, but these have been eliminated or minimized as subsequently described.

Partially as a result of the change in professional location of the principal investigator (which produced some knotty and time-consuming financial and technical problems) and partially due to the fundamental nature of natural water systems, the electrode-electrolyte system to be employed underwent rather radical changes in the final three months of the investigation. The original choice--rotating platinum in a sulfosalicylic acid electrolyte medium--was finally abandoned, since (1) the rotating platinum electrode appeared incapable of yielding, reproducibly, the level of separation and sensitivity desired (particularly for iron) and (2) the sulfosalicylic acid medium prevented analysis for lead, one of the most important metals considered, in our judgment, while the analysis for iron was nearly as unsatisfactory. For a time, it appeared that the dropping mercury electrode might suffice in the same medium and, in fact, the prototype instrument was designed around this concept. However, the results of field testing and the inability of the system to permit determination of lead convinced us that a different electrolyte was necessary. Although some problems were encountered in the field use of the DME, they were resolved so that the DME was retained in the final instrument.

The electrolyte ultimately selected for Model II of the instrument, after several other possible electrolytes were tested, was trisodium citrate. This salt was selected, not only because it would serve as a satisfactory electrolytic medium for the determination of lead, cadmium, zinc, and iron, but also for its buffering and complexing capacities in acidic solutions. After appropriate preliminary studies, a 0.02

molar solution of the salt was selected as the supporting electrolyte, to which the sample was to be added. Initially, a concentration of 0.001% Triton X-100 was also added to the citrate medium as a maximum suppressor; subsequent tests proved that the maximum suppressor was not required at the metallic ion concentrations involved in natural waters analyses and it was eliminated from further testing and method development. Although the citrate medium precludes the determination of copper (due to masking of the copper wave by the electrolyte anodic wave), it does permit the determination of lead, cadmium, zinc and iron; nickel does not yield a polarographic wave in this medium and chromium does not interfere in concentrations up to about 0.2 ppm--a concentration considerably larger than that commonly found in natural waters. Applicability of the instrument to other metal ion determinations is discussed subsequently, as are other problems associated with the electrode-electrolyte system. After the latter system was selected, the final design and construction of the basic instrument could be approached.

Fundamental Circuitry.--A number of prerequisite characteristics were considered prior to designing the final instrument, once the nature of electrode and electrolyte were established. These characteristics included: (1) appropriate compromise between instrument sensitivity and field reliability, (2) adaptability of the circuitry to the electrode system, (3) relative simplicity and convenience of field operation, and (4) field maintenance.

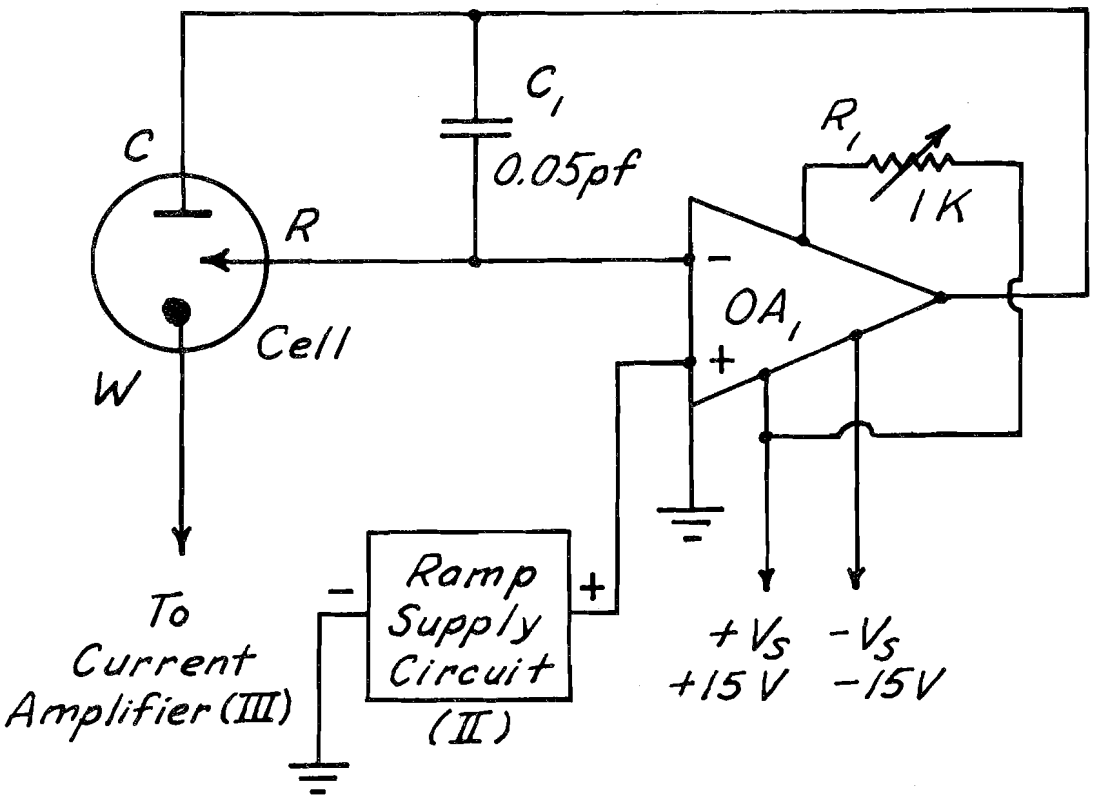
The design eventually adopted consists of six individual circuits,

each designed and interconnected so as to produce an operational whole compatible with the previously enumerated characteristics. These individual circuits include: (1) the 3-electrode operational amplifier circuit (Figure 1), whose basic function is to furnish the desired applied potential to the electrode system in the polarographic cell, as supplied from (2) the ramp supply circuit (Figure 2); the latter permits the proper pre-determined voltages (based on the nature of the working electrode, electrolyte, and electroactive species) to be selected by an appropriately constructed manual control; (3) the current-to-voltage converter and amplified circuit (Figure 3), which amplifies and converts the current output from the test cell so that it may be subsequently measured; (4) the current compensation circuit (Figure 4), designed so that the polarographic residual currents may be compensated for, thus permitting simple manual measurement of the waves via the two-point manual measurement technique; (5) the output circuit (Figure 5), which permits the desired signal to be measured by way of the read-out milliammeter; and (6) the battery test circuit (Figure 6), which allows field testing of the condition of the various batteries involved in powering the entire device--the advantage of battery operation for field use also introduces the disadvantage of battery decay and the necessity for eventual replacement.

Figure 7 illustrates the mode by which these six fundamental circuits have been interconnected to produce the final operational instrument. A relatively detailed listing of the electrical and electronic components required to assemble the device is given in Table 1;

Figure 1

3-Electrode Operational Amplifier Circuit (I)



C Counter Electrode (Pt)
R Reference Electrode (SCE)
W Working Electrode (DME)

Figure 2

Ramp Supply Circuit (II)

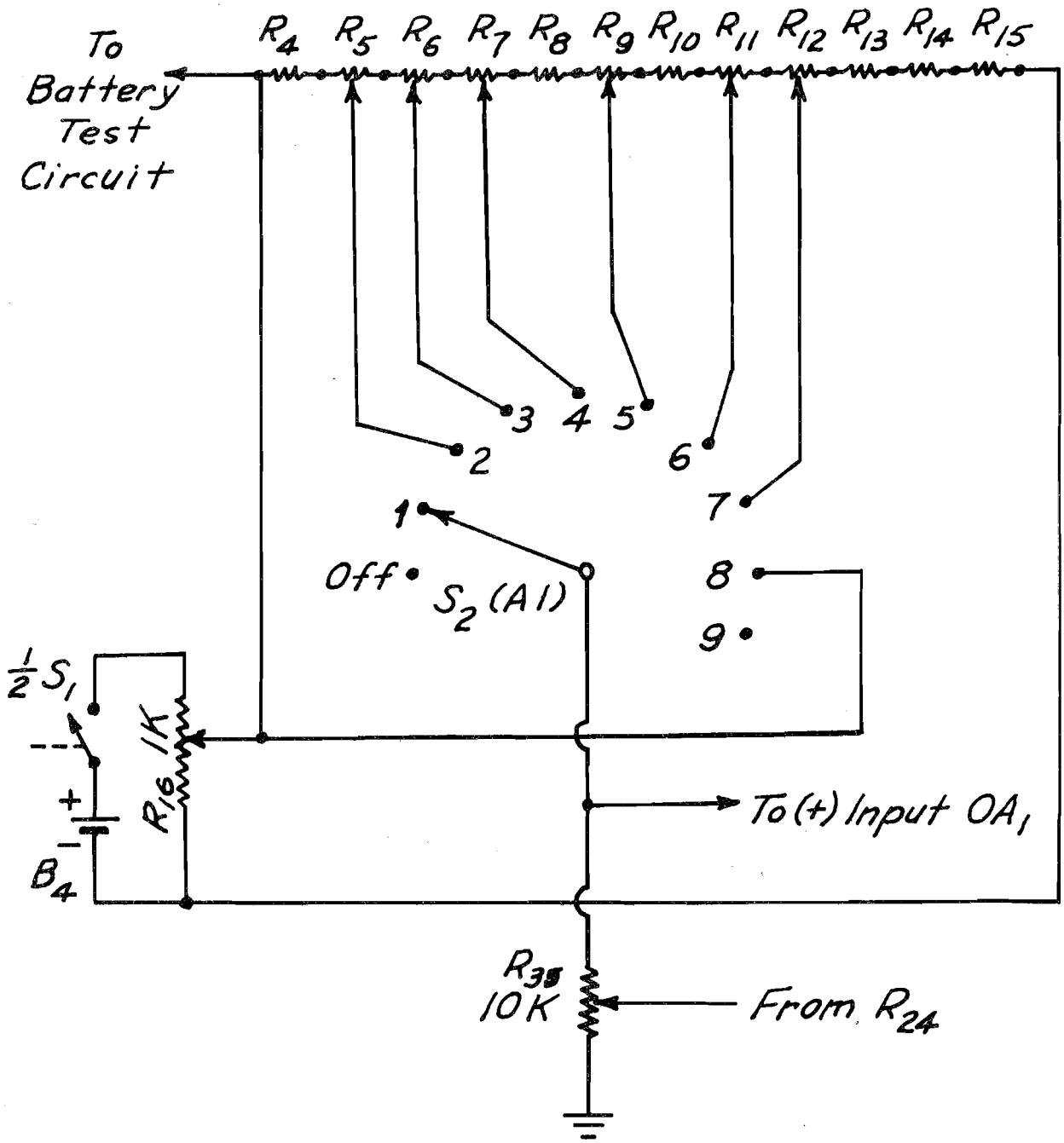
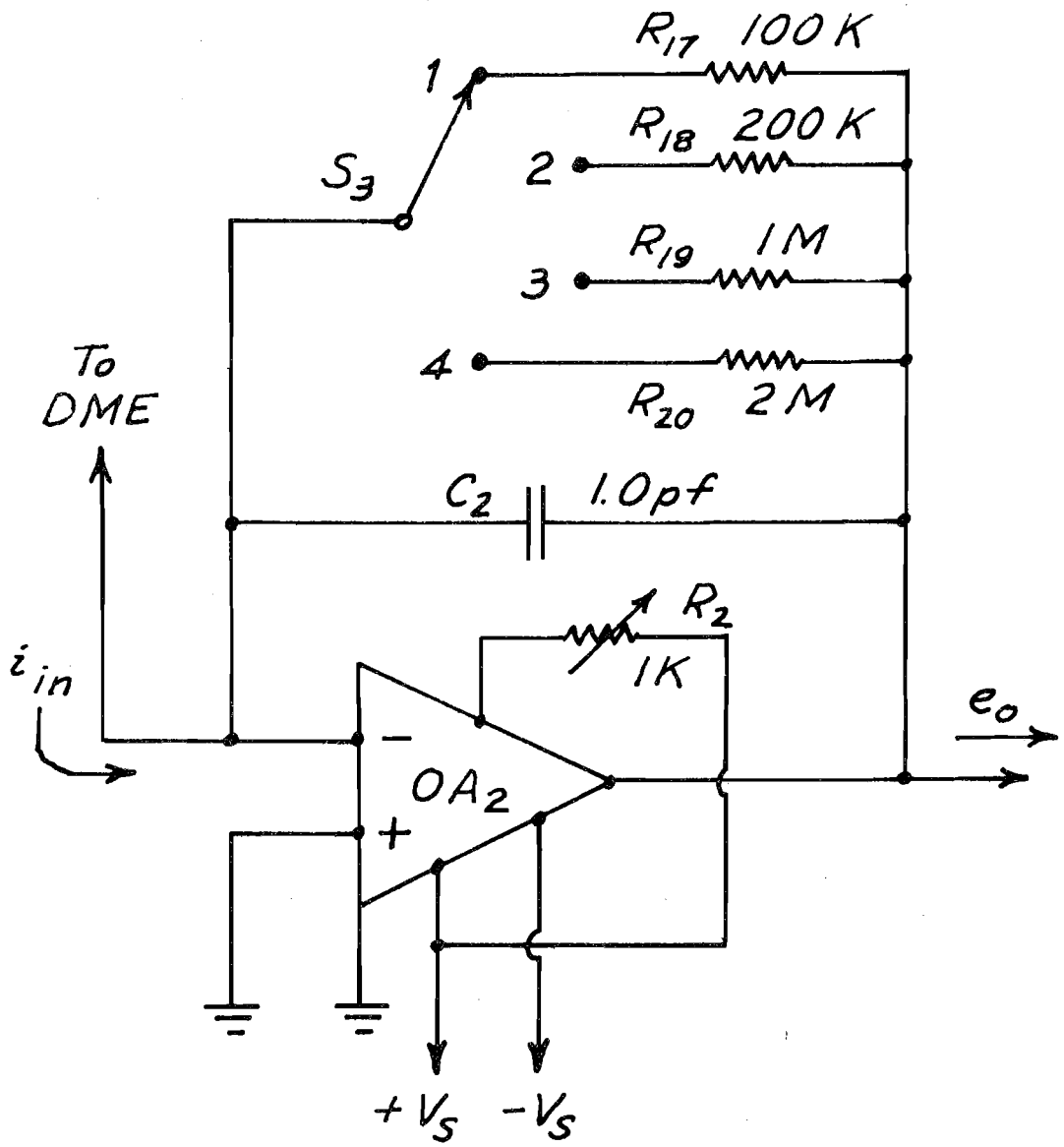


Figure 3

Current - to - Voltage
Converter and Amplifier Circuit (III)

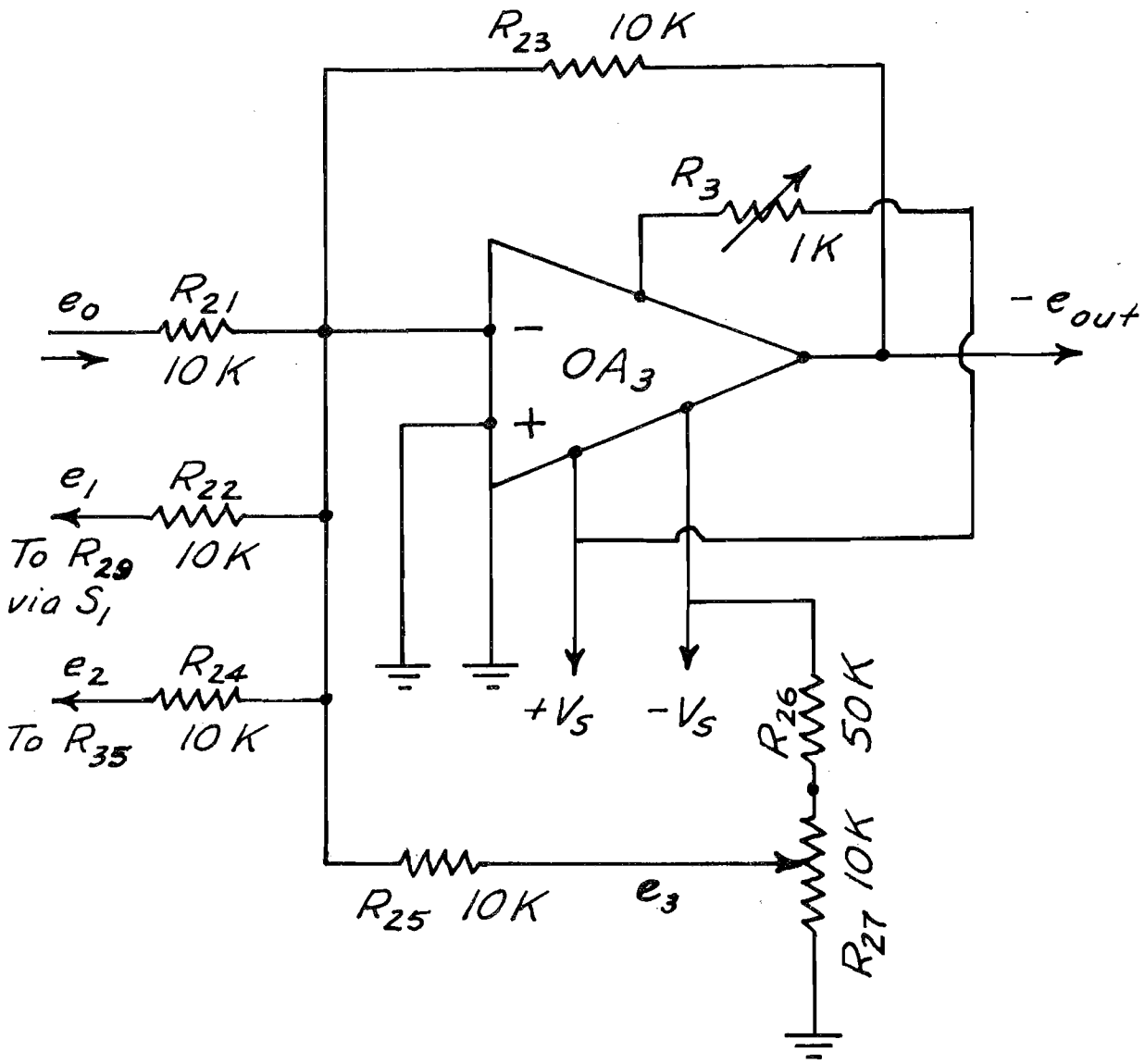


$$e_o = i_{in} R_f$$

where R_f = feedback R = R_{17-20}

Figure 4

Current Compensation Circuit (IV)



$$\text{Amplifier gain} = \frac{-R_f}{R_{in}} = -\frac{10K}{10K} = -1$$

$$e_{out} = -(e_0 + e_1 + e_2 + e_3)$$

Figure 5

Output Circuit (V)

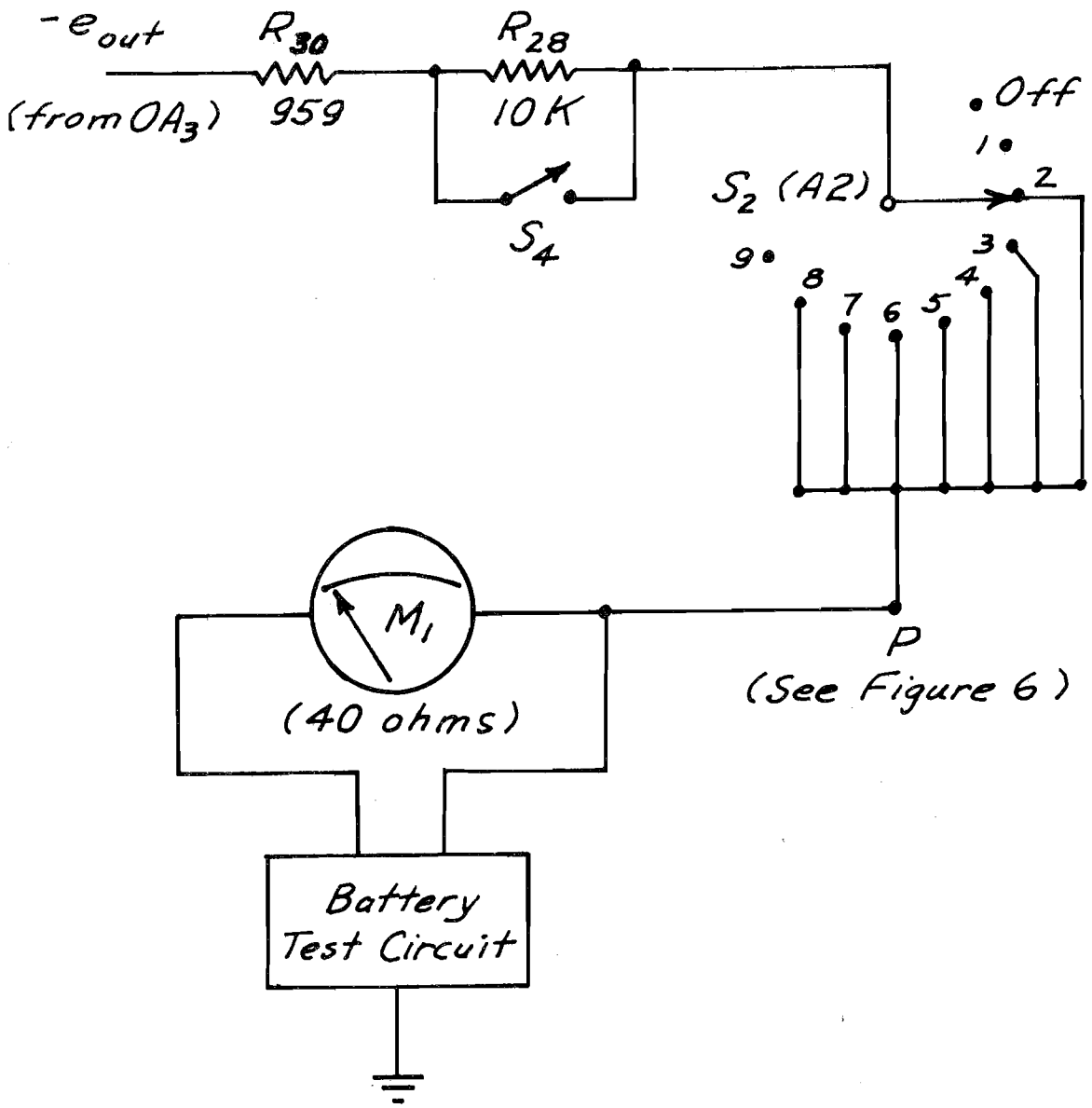


Figure 6
Battery Test Circuit (VI)

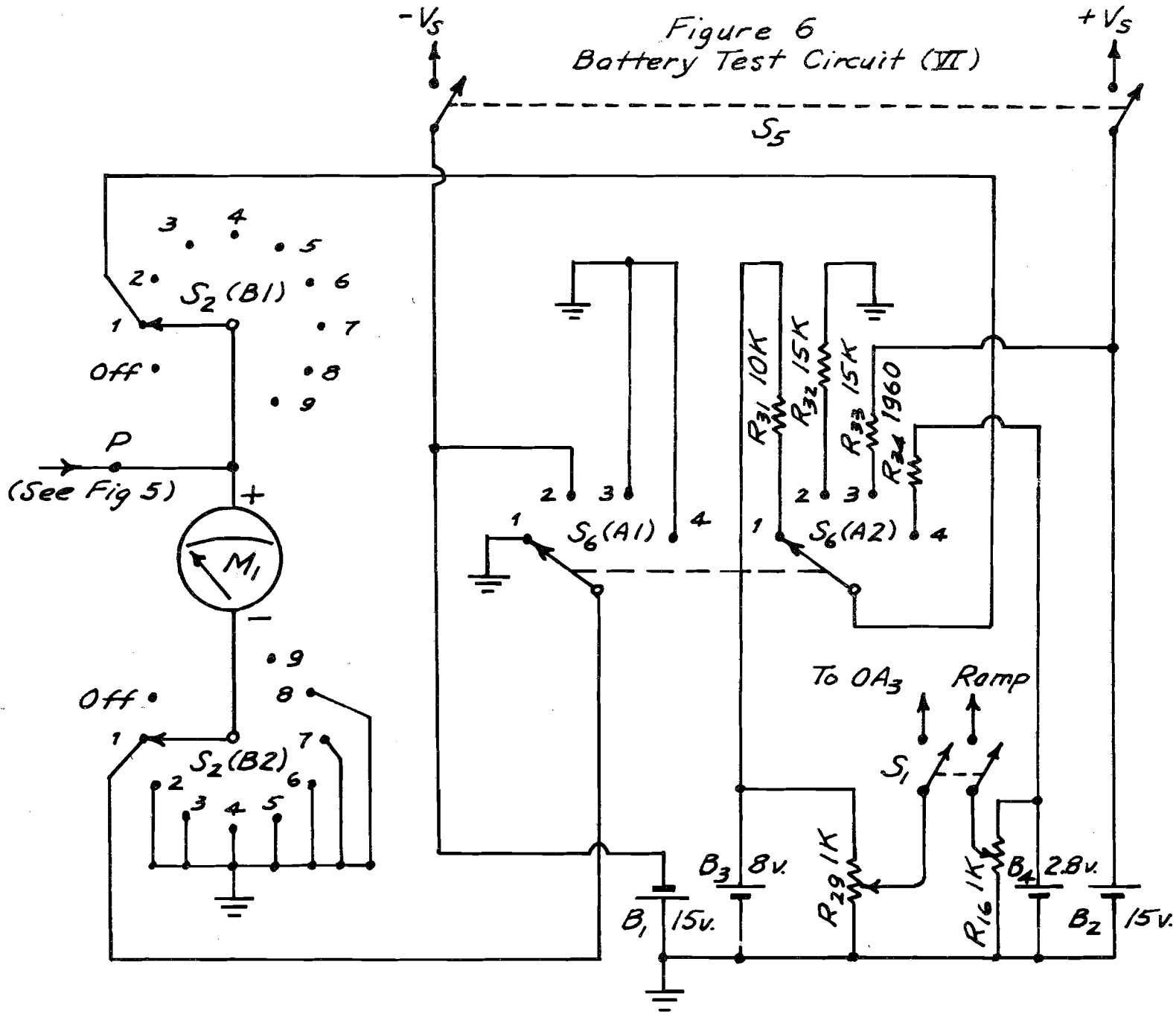


Figure 7

Composite Diagram

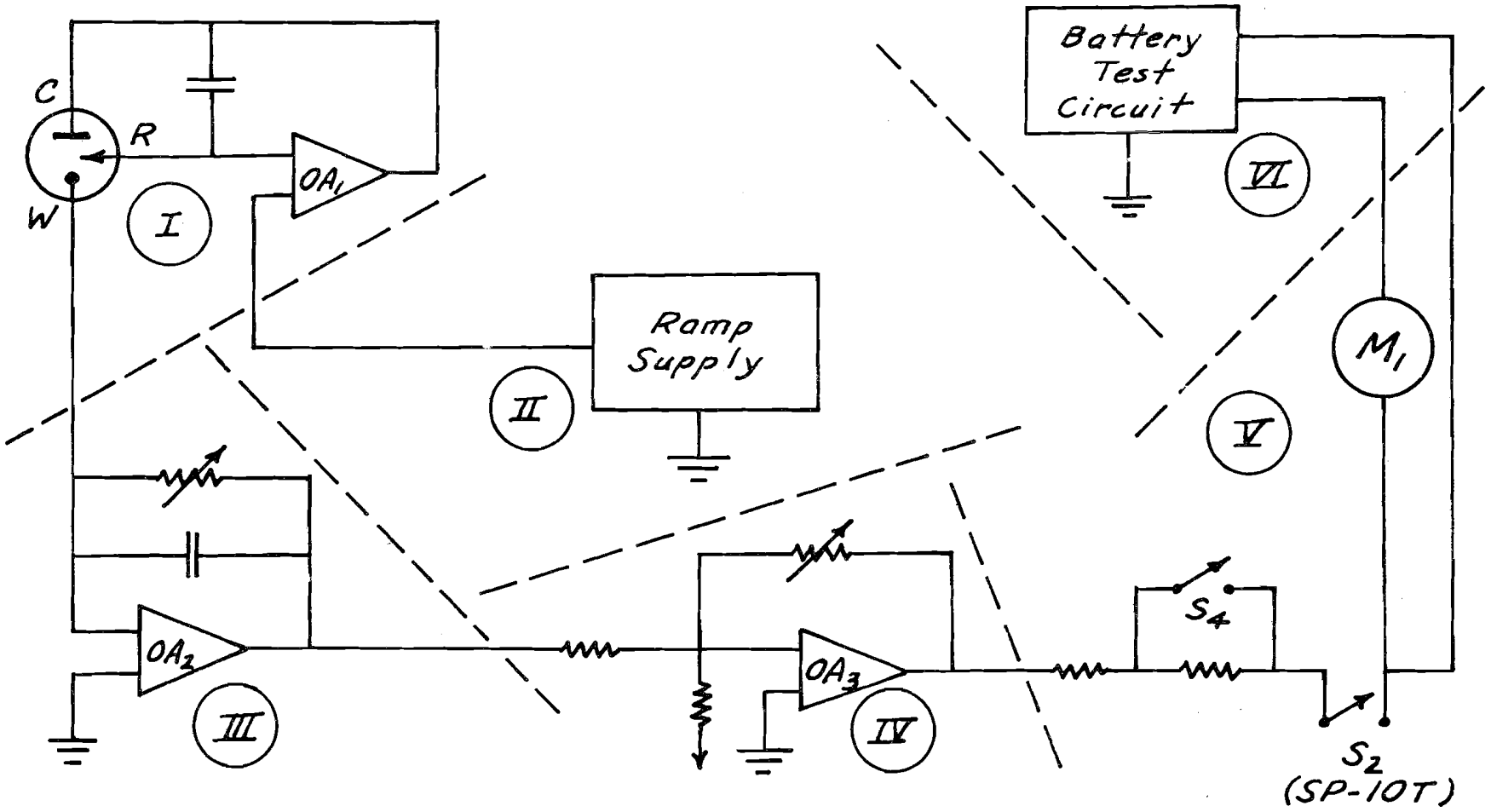


Table 1

Water Analyzer--Electrical Components

C	Counter electrode; 2-inch length of 22-gauge platinum wire.
R	Reference electrode; Sargent-Welch S-30080-17 saturated calomel electrode.
W	Working electrode; dropping mercury electrode.
C_1	Capacitor, 0.05 pf, 50 WVDC.
C_2	Capacitor, 1.0 pf, 50 WVDC.
OA_{1-3}	Operational amplifiers, Analog Devices (221 Fifth St., Cambridge, Mass. 02142) Model 142A, with AC1003 sockets.
M_1	Milliammeter, Simpson Wide-Vue Panel, 0-1 mA DC, Model 1329, 4 1/2-inch, with matching bezel.
S_1	Switch, Lev-R, Switchcraft Type 28204, DPST, locking.
S_2	Switch, JBT Type 20M-2103N, 3-deck, 2 poles/deck.
S_3	Switch, Mallory Type 3134J, 3-pole, 4-position, shorting.
S_{4-5}	Switches, Lev-R, Switchcraft Type 28204, non-locking.
S_6	Switch, Mallory Type 3234J, 3-pole, 4-position, non-shorting.
B_{1-2}	Batteries (2), Burgess Type K10, 15VDC, with Keystone No. 166 holders.
B_3	Batteries (2), Mallory Type TR233R, 4.05 VDC, with Keystone No. 173 holders.
B_4	Batteries (2), mercury, Mallory Type RM12R, 1.35 VDC, with Keystone No. 140 holder.
R_{1-3}	Trimpots, 1K ohms, IRC Type 60-20.
R_4	Resistor, 70 ohms, 1/2-watt, 20%.
R_{5-14}	Trimpots, 100 ohms, Bourne Type 273.
R_{15}	Resistor, 20 ohms, 1/2-watt, 20%.
R_{16}	Potentiometer, 1K ohms, 2-watt, Ohmite Type CV-1021, linear taper.

Table 1 Continued

R_{17}	Resistor, 100K ohms, 1%.
R_{18}	Resistor, 200K ohms, 1%.
R_{19}	Resistor, 1M ohms, 1%.
R_{20}	Resistor, 2M ohms, 1%.
$R_{21-25, 31}$	Resistors, 10K ohms, 1%.
R_{26}	Resistor, 50K ohms, 1/2-watt, 20%.
$R_{27, 35}$	Potentiometers, 10K ohms, 5-watt, Centralab Type WN-103, linear taper.
R_{28}	Resistor, 10K ohms, 1/2-watt, 20%.
R_{29}	Potentiometer, 1K ohms, 10-turn, IRC Type 5000.
R_{30}	Resistor, 959 ohms, 1%.
R_{32-33}	Resistors, 15K ohms, 1%.
R_{34}	Resistor, 1960 ohms, 1%.
	Instrument case, Bud Type TC-304, with Retracto-link Type 2093 handle.
	Miscellaneous: plugs, connectors, dial plates, switch guards, terminal strips, wiring, etc.

miscellaneous parts, such as knobs, dials, labels, clips, terminals, etc., are not detailed. The total single-item purchase cost of the electrical, electronic, and ancillary components was about $300 at the time of their original procurement. Figure 8 simply indicates the geometry and surface location of the various controls eventually referred to in the Instrument Operating Procedure. Figure 9 shows a rear view of the instrument, closed for travel except for the rear-access battery compartment, which is opened as it would be for replacement of the batteries.

Polarographic Test Cell.--A polarographic test cell was designed which would be suitable for use in a portable instrument. The cell (Figure 10) consists of a 1-inch outside diameter glass vessel 1 1/4 inches tall, fitted with a nylon cover machined so as to fit into the vessel; the cover contains access holes for the commercial saturated calomel reference electrode (SCE), the dropping mercury electrode capillary (DME), the platinum wire counter electrode (Pt), and a gas bubbler tube for preliminary oxygen purging. The capillary was made from a Sargent-Welch 2-5 second capillary, connected to the mercury reservoir with a short length of Tygon tubing. The mercury reservoir, which was a source of difficulty during testing of the prototype, was redesigned to eliminate the back-pressure problem and permit much simpler and more foolproof operation of the electrode. A Cole-Parmer polyethylene gas sampling tube (125 cc capacity, 4 1/2 inches long) was modified by cutting the chamber length to 1 1/4 inches and re-sealing the stopcock thus removed onto the cut end with epoxy cement,

Figure 8

Instrument Panel

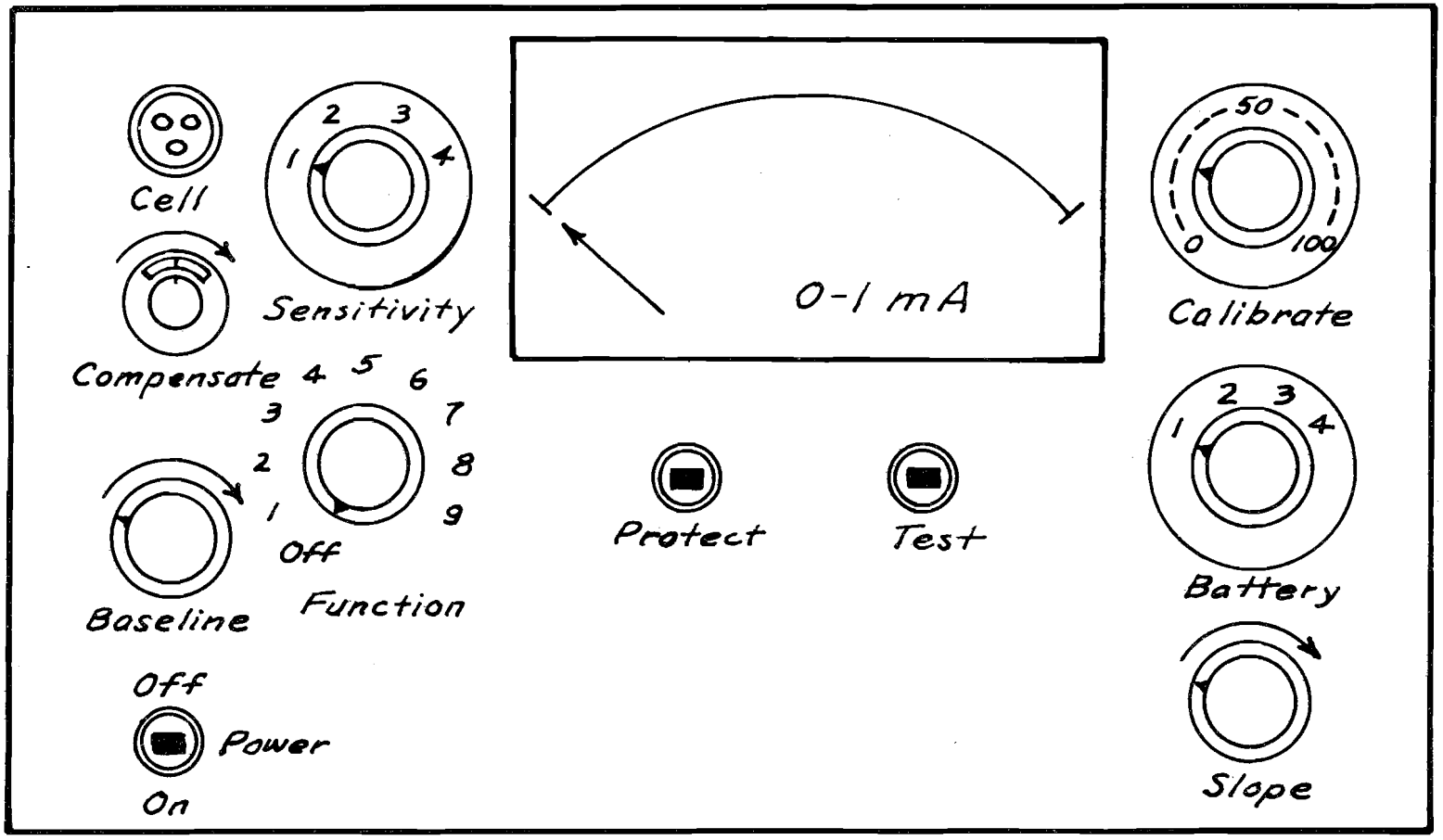


Figure 9

Polarographic Test Cell

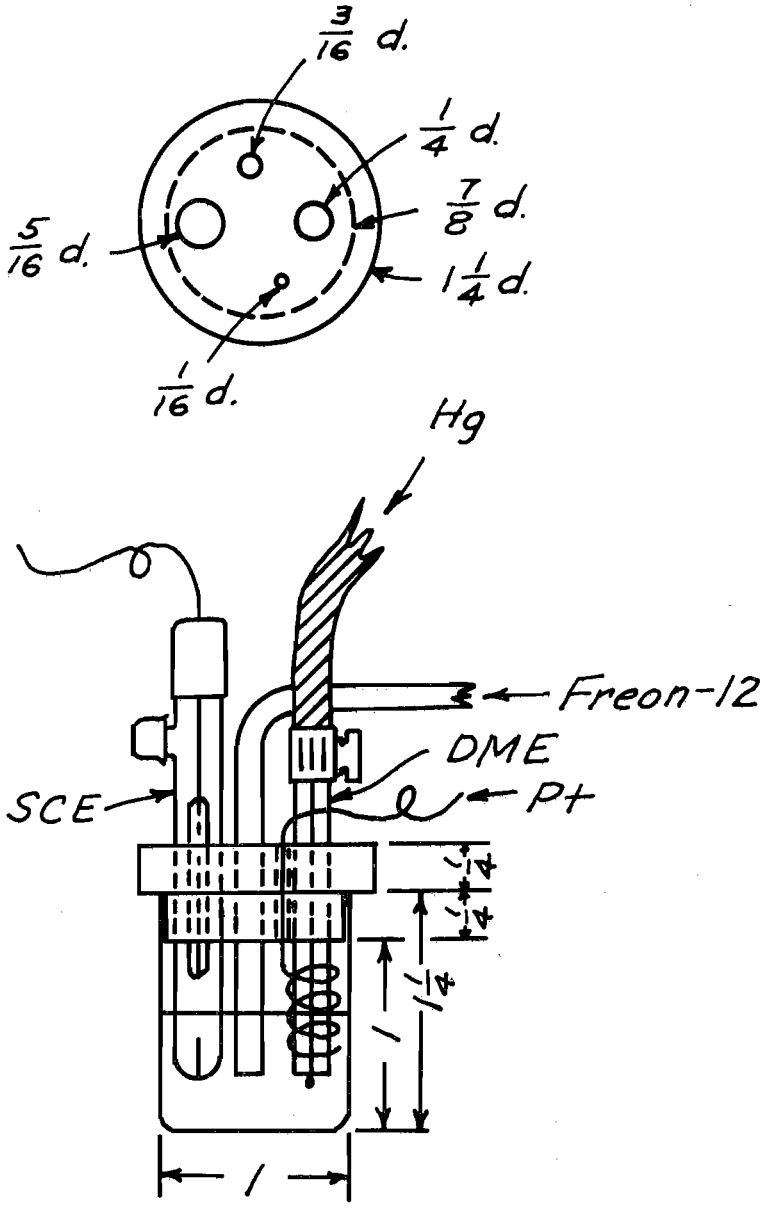
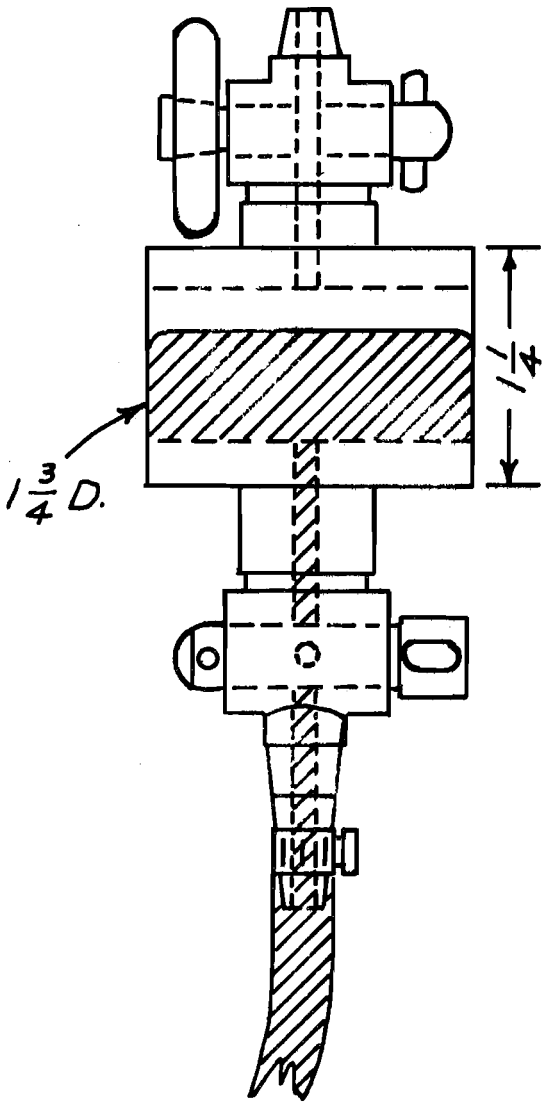


Figure 10

DME Mercury Reservoir

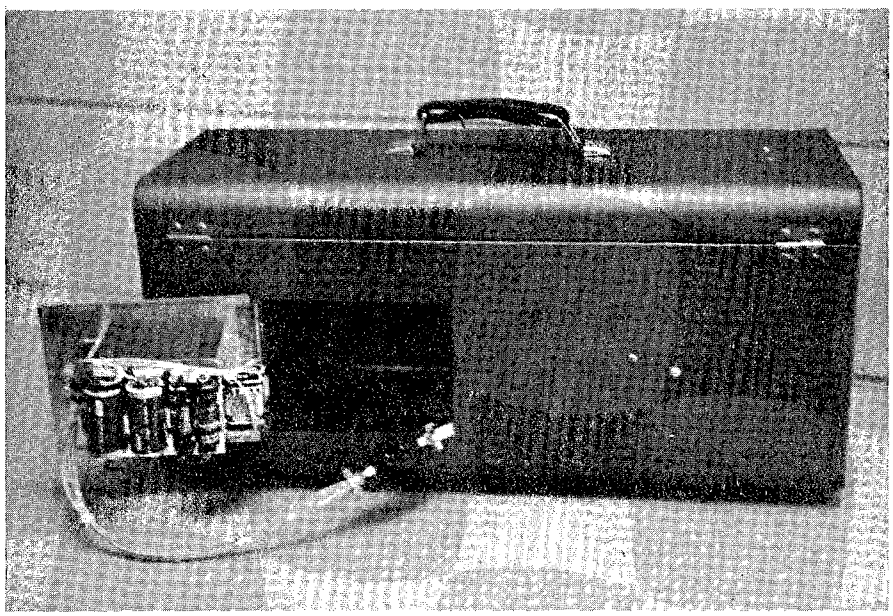


after rotating the stopcock 180° from its original orientation. Thus, the stopcock handles are on opposite sides of the barrel of the reservoir, as shown in Figure 11. The polyethylene reservoir is of such dimensions that it fits conveniently, mounted in an ordinary kitchen broom clip, inside the cover of the instrument case. The stopcocks are mercury-tight, so that they may be closed for storage and travel, but easily opened for operation.

Oxygen-Purging Apparatus.--The question of measurement and/or removal of dissolved oxygen is always pertinent to aqueous polarographic techniques, owing to the well-known polarographic reduction waves for the dissolved gas. Some early consideration was given to incorporating an oxygen-measuring system (such as the Beckman Dissolved Oxygen Electrode System) into the instrument. However, due to the availability of several excellent D. O. kits, it was decided that this measurement should not be included. The removal of dissolved oxygen prior to polarographic measurement of the metal ions had to be accomplished, however. This fact accounts primarily for the extensive early efforts to employ the sulfosalicylic acid electrolyte system described in earlier reports. In that system, a basic medium could be employed, which permitted convenient oxygen scavenging through the simple addition of solid sodium sulfite prior to the polarographic measurement. As previously mentioned, however, this system precluded measurement of lead, and was abandoned.

The alternative to basic sulfite purging was the use of nitrogen or some other insoluble gas. Although small 'lecture' tanks of nitrogen gas and suitable gauges may be obtained easily, they are

Figure 11



Rear view of closed instrument case

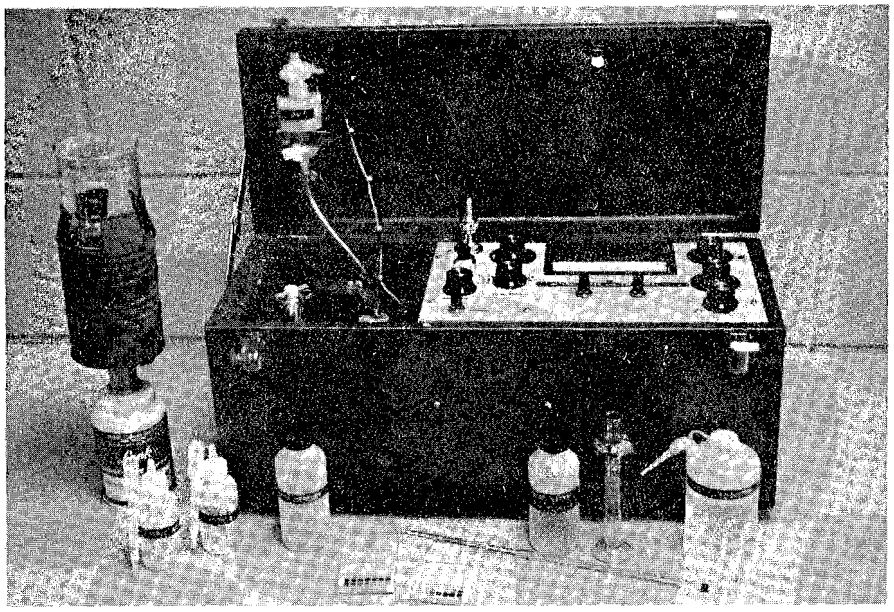
with battery compartment open.

relatively expensive, relatively heavy (for incorporation into a portable device), and certainly not readily available in the field. In searching for a suitable substitute for nitrogen, propane was first tried (since, as subsequently described, a can of propane or similar gas is incorporated in the instrument case as fuel for the sample concentration burner), but this gas was found to be unsatisfactory in this case.

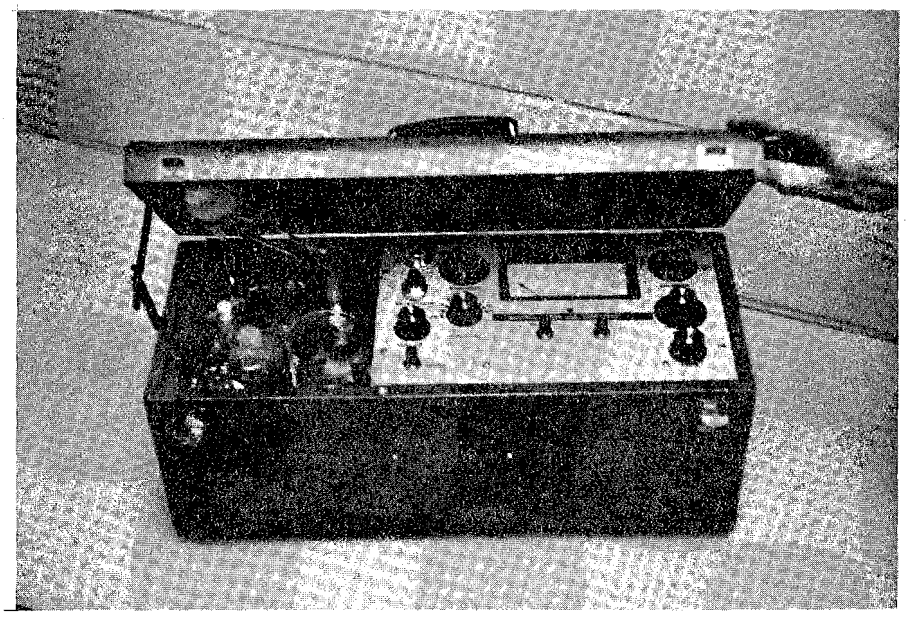
Then Freon-12 was studied; this gas proved to be eminently satisfactory, as shown by comparative results for purging with nitrogen or freon (Figure 12). It is also readily adaptable to a field device, owing to the ready availability of inexpensive (less than $1) 15-ounce throw-away (in proper receptacles, of course!) containers of Freon-12. These cans, along with a convenient and necessary dispensing valve for repeated use with any size can of the refrigerant, are available from most automotive supply stores--they are marketed normally for rejuvenation of automobile air-conditioning units.

Pre-Concentration Apparatus.--Subsequent to field testing of the prototype Model I, it became obvious that a readout device much less sensitive than a 0-20 microammeter should be employed for the instrument, if it was to withstand the relatively rough treatment it might receive in the field. Substitution of a 0-1 milliammmeter with appropriate electronic signal amplification was a partial solution, but some sacrifice in sensitivity had to be accepted. The end result was the decision to incorporate pre-concentration of samples--a necessity in any case for some types of samples, due to the fact that pre-concentration

Figure 12



Completed analyzer, with accessories removed from case.



Analyzer with accessories packed for travel.

with added nitric acid can destroy some organic species which might interfere with eventual polarographic analysis. Consequently a field pre-concentration apparatus was devised (Figure 13). This device consists of a beaker holder, made from an ordinary 'tin' can, and a Lenk LP laboratory burner with Meker-type flame adapter (Dynalab Corporation, Box 112, Rochester, New York 14601); a graduated 250-ml beaker is used as the sample container. A 28-ounce food can, e. g., a family-size Campbell's Pork and Bean can, fits conveniently over the base plate of the Lenk burner and can be easily converted, as shown in Figure 13, into a suitable beaker holder. The Lenk burner fits any of several brands of LP fuel cans available in 6-ounce throw-away cans from most sporting goods stores--they are commonly used as fuel for single-burner camp stoves. The beaker holder was painted with ultra high temperature automotive paint. The procedure adopted for pre-concentration of water samples is described subsequently in another section of the report.

Completed Analysis Kit.--Photographs of the completed instrument, open for operation with accessory apparatus, containers and other materials, as well as prepared for travel are shown in Figure 14. If desired, a somewhat larger instrument case could be used, allowing more space for transportation of additional equipment, such as sampling bottles, test kits for dissolved oxygen or other components of water samples not measurable with the instrument described, etc.

ANALYTICAL METHOD DEVELOPMENT

Introduction.--Preliminary studies of chemical electrolyte systems

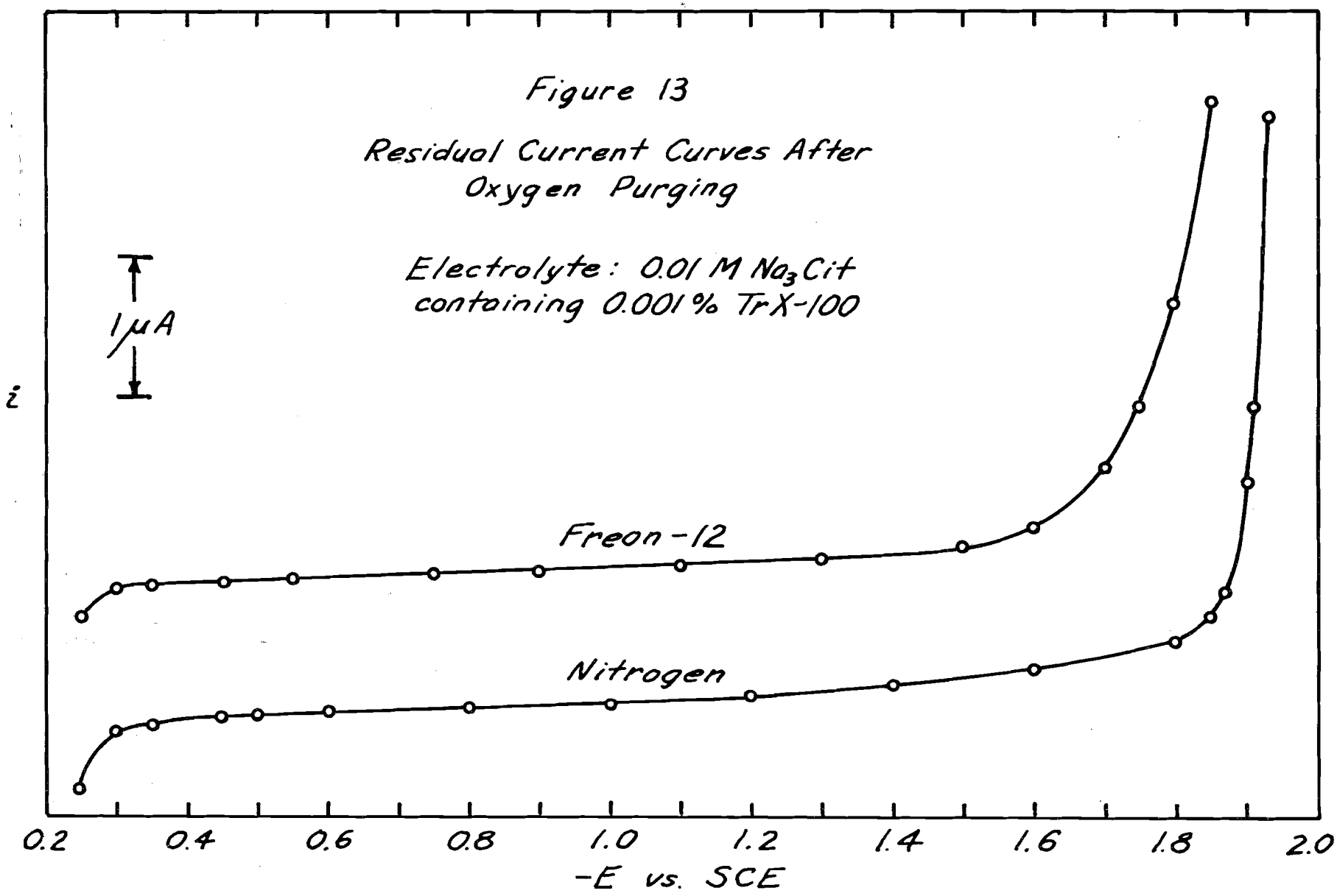


Figure 13
Residual Current Curves After Oxygen Purging
Electrolyte: 0.01 M Na3Cit containing 0.001% TrX-100
1 μA
i
Freon-12
Nitrogen
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
-E vs. SCE

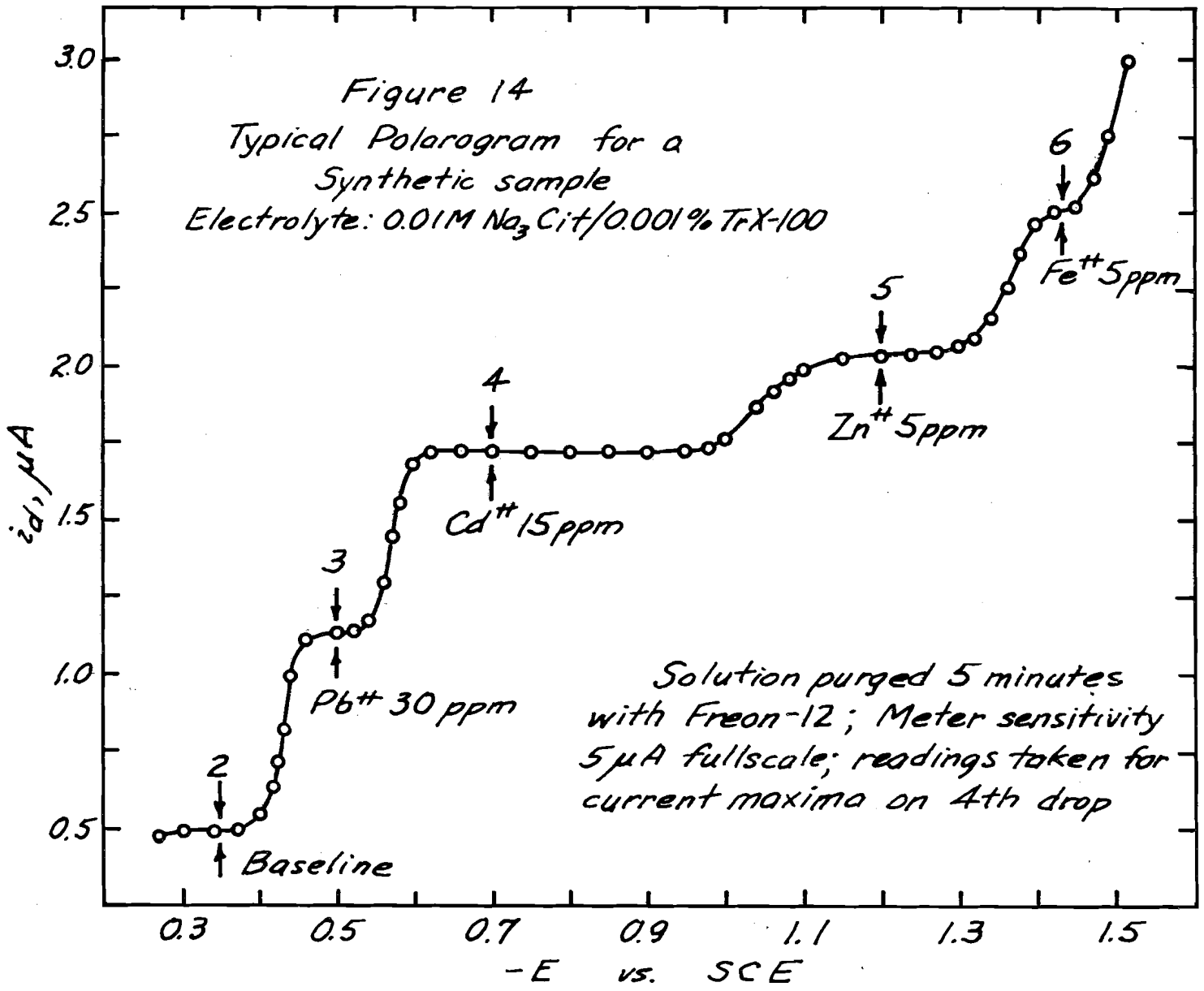


Figure 14
Typical Polarogram for a
Synthetic sample
Electrolyte: 0.01M Na3Cit/0.001% TrX-100
3.0
2.5
2.0
1.5
1.0
0.5
id, μA
0.3
0.5
0.7
0.9
1.1
1.3
1.5
-E vs. SCE
2
Baseline
3
Pb++ 30 ppm
4
Cd++ 15ppm
5
Zn++ 5ppm
6
Fe++ 5ppm
Solution purged 5 minutes
with Freon-12; Meter sensitivity
5μA fullscale; readings taken for
current maxima on 4th drop

containing various metal ions eventually resulted in the selection, as previously mentioned, of sodium citrate as the most suitable electrolytic medium for use with the instrument and electrode systems which had, by this time, been constructed. This electrolyte is not an ideal one, inasmuch as only four of the ions of interest (Pb^{++}, Cd^{++}, Zn^{++}, and Fe^{+++}) may be measured in it, but no other electrolyte of the several tested was as suitable. The advantages of the citrate medium are that (1) each of the four ions mentioned gives a reasonably well-defined wave; (2) the waves are easily separable, so that the two-point polarographic measurement technique is feasible; (3) the salt complexes Fe^{+++} so that its wave does not interfere with that for Zn^{++}; and (4) the citrate ion serves, with the excess hydronium ion remaining after preconcentration, to maintain the system in the pH range required to prevent interference from hydrogen discharge with the iron wave. No maximum was observed in metal ion concentrations up to 50 ppm in the test solution, as previously indicated.

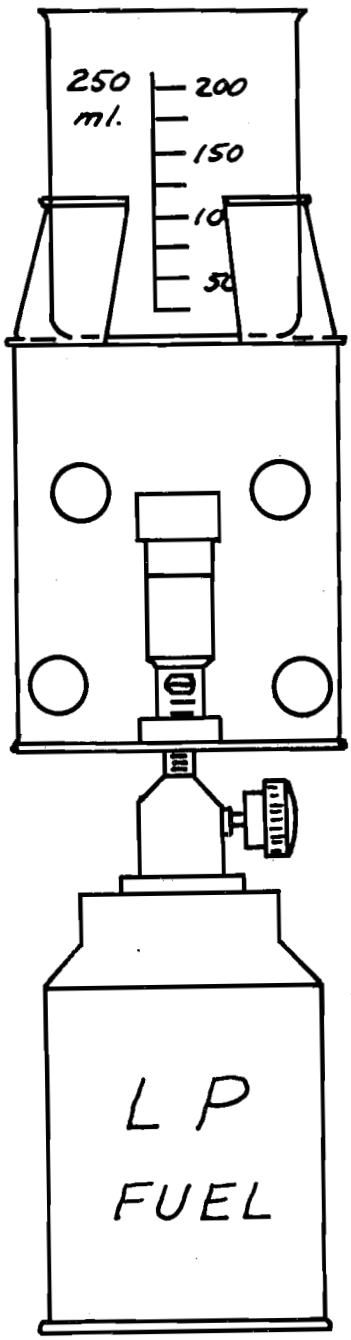
Stock and Test Solutions.--For preliminary exploratory purposes, a number of stock metal ion solutions (Cu^{++}, Pb^{++}, Zn^{++}, Cd^{++}, Ni^{++}, Cr^{+++}, Mn^{++}, and Fe^{+++}) were prepared from their pure perchlorates; these solutions were standardized via potentiometric titration with previously standardized EDTA. Test solutions and synthetic water samples were then prepared by mixing appropriate volumes of the stock solutions with the desired volume of 0.2 molar sodium citrate (a final test solution concentration of 0.02 molar sodium citrate was found to be optimum for the measurements made). The test solutions thus prepared

were then placed in the polarographic cell, purged of dissolved oxygen (initially with nitrogen, later with Freon-12) for five minutes and polarographed; polarograms were initially recorded with a Series 401 Heath Polarography System; eventually, after the addition to the instrument of a variable applied potential mode, the polarograms were recorded manually with the instrument itself. A typical example of a polarogram so recorded is shown in Figure 15.

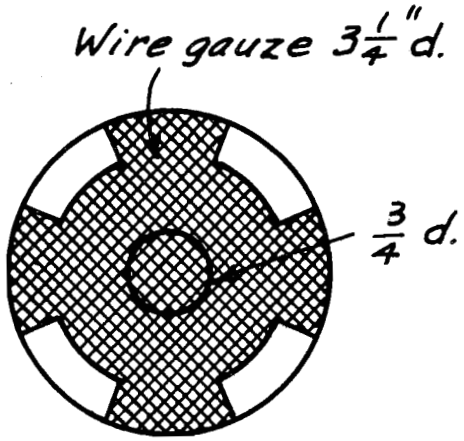
Polarographic Analytical Measurements.--Based on the location and nature of the polarographic waves for the four cations in the citrate medium ($E_{1/2}$ values vs. SCE: -0.43 for Pb^{++}, -0.57 for Cd^{++}, -1.03 for Zn^{++}, and -1.36 for Fe^{+++}), potentials were selected for two-point measurement of wave heights. These potentials (vs. SCE) were: Baseline, -0.35; Pb^{++} wave, -0.50; Cd^{++} wave, -0.70; Zn^{++} wave, -1.20, and Fe^{+++} wave, -1.43. The ramp circuit trimpots R_{5-14}, Figure 2, were then adjusted with the aid of an externally connected vacuum tube voltmeter so that the applied voltages picked off with the Function Switch S_2 were the values shown in Figure 15 (indicated by the vertical arrows, with corresponding Function Switch position numbers). Initially, the direct wave height comparison measurement technique was attempted, i.e., the height of a wave was determined by the difference in polarographic current measurement at two successive Function Switch positions; the concentration of the ion responsible for the wave was then determined by reference to a calibration curve (measured current vs. concentration). However, for the very small concentrations frequently encountered in water samples, these measurements all too frequently were of the same

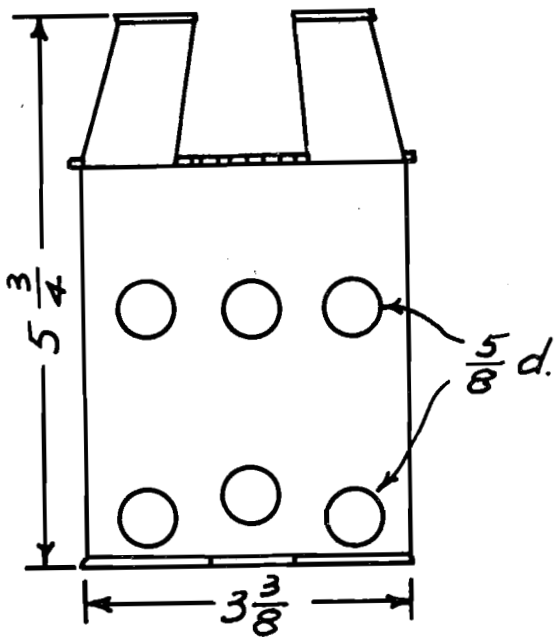
Figure 15

Sample Concentration Burner Assembly



Complete Assembly





Beaker Holder

magnitude as the observed experimental error of the measurement. For this reason, the well-known standard addition technique was selected for ultimate quantitative measurements, so that even the smallest currents measured might be large enough to minimize experimental error.

Standard Addition Procedure:--If two polarographic test solutions are prepared in the same total volume, one containing a known concentration of an electroactive species, C_s, and the other the known concentration plus an added (but unknown) amount of the same ion, $C_s + C_x$, and the polarographic currents are recorded for each solution separately, the relationship of the wave heights measured to the concentrations is:

$$\frac{C_s}{C_s + C_x} = \frac{i_s}{i_{s+x}}$$

where i_s is the wave height for the solution containing standard only, and i_{s+x} is the wave height for the solution containing standard plus unknown. If the original sample has been pre-concentrated prior to polarographic measurement, the concentration in the original unconcentrated solution may be represented by C_x, while that measured in the actual test solution becomes $F.C_x$, where F is a concentration factor, i.e., if the sample were pre-concentrated from 100 ml to 10 ml, F = 10 and $F.C_x = 10C_x$. Then, the results of the experimental measurement may be represented as

$$\frac{C_s}{C_s + FC_x} = \frac{i_s}{i_{s+x}}$$

from which

$$C_x = \frac{C_s(i_{s+x} - i_s)}{F.i_s}$$

This relationship lends itself admirably to the two-point method of polarographic quantitative analysis if a suitable standard solution is available. For the present work, on consideration of the natures of the various polarographic waves involved, the composition of a suitable multiple-ion standard solution was found to be that given in Table 2--on dilution in the final test solution, the standard concentrations are shown as Test Solution Concentrations in the table. The standard water was prepared so that 1.0 ml, on dilution to 10 ml would contain, not only the desired cations in the proper concentrations, but also the pre-determined concentration of supporting electrolyte. Thus, successive measurement of wave heights as previously described, leads to experimental data of the type shown at the top of Table 3. Sample calculations for such data, by the standard addition relationship, are also indicated in Table 3 for Sample II only.

One of the advantages of the current compensation circuit (Figure 4) is also illustrated by the data in Table 3. The current measurement at Function Switch Position 6 for Sample II was offscale; therefore, the Compensate Control was adjusted so that a current could be read at position 6 (6.80); then the Function Switch was reset to position 5, where a new reading (3.90) was made, and the calculation completed as indicated in Table 3. The calculations for an unconcentrated sample are identical, except for the change in the value of the concentration factor, F (see footnote, Table 4). As a result of the type of measurement just described, an Instrument Operating

Table 2

Standard Water Composition; Test Solution Preparation

Component	Standard Concentration[a]	Test Solution Concentration
	ppm	ppm
Pb^{++}	300.0	30.0 + x[b]
Cd^{++}	150.0	15.0 + x
Zn^{++}	50.0	5.0 + x
Fe^{+++}	50.0	5.0 + x
Na_3Citrate	0.20 M	0.02 M

[a] Metal ion stock solutions prepared from pure metallic perchlorates, followed by standardization by titration with EDTA; water standard prepared by proper mixing and dilution.

[b] x = concentration of metal ion from unknown sample.

Test Solution Preparation

Test solutions are prepared by mixing 1.0 ml (pipet) of standard water with 8-9 ml of pre-concentrated sample, followed by dilution to 10 ml with distilled water and oxygen-purging with Freon-12 prior to measurement.

Table 3

Calculation of Results

	Meter Readings[a]				
Function Switch Position:	2	3	4	5	6
Applied Voltage Value:	-0.35	-0.50	-0.70	-1.20	-1.43
Measurement of:	Base	Pb^{++}	Cd^{++}	Zn^{++}	Fe^{+++}
I. Standard Water	0.40	2.05	3.45	4.15	5.80
II. Sample[b] + Standard	0.40	3.75	6.45	7.95 3.90[c]	-- 6.80
III. Sample[d] + Standard	0.40	2.25	3.85	4.75	6.55

[a]Meter read to nearest 0.05 units on 4th mercury drop maximum current.

[b]Sample pre-concentrated from 100 ml. to 10 ml.

[c]Compensated; original reading for Function Switch Position 6 offscale.

[d]Unconcentrated sample.

Calculations

I. Standard Water: $C_{Pb} = 30.0$; $i_{Pb} = 2.05 - 0.40 = 1.65$ (3 - 2)

$C_{Cd} = 15.0$; $i_{Cd} = 3.45 - 2.05 = 1.40$ (4 - 3)

$C_{Zn} = 5.0$; $i_{Zn} = 4.15 - 3.45 = 0.70$ (5 - 4)

$C_{Fe} = 5.0$; $i_{Fe} = 5.80 - 4.15 = 1.65$ (6 - 5)

II. Sample + Standard:

$$i_{Pb + x} = 3.75 - 0.40 = 3.35$$

$$i_{Cd + x} = 6.45 - 3.75 = 2.70$$

$$i_{Zn + x} = 7.95 - 6.45 = 1.50$$

$$i_{Fe + x} = 6.80 - 3.90 = 2.90$$

Results:

$$C_{Pb} = \frac{30.0(3.35 - 1.65)}{10(1.65)} = 3.15 \text{ ppm}$$

$$C_{Cd} = \frac{15.0(2.70 - 1.40)}{10(1.40)} = 1.39 \text{ ppm}$$

$$C_{Zn} = \frac{5.0(1.50 - 0.70)}{10(0.70)} = 0.57 \text{ ppm}$$

$$C_{Fe} = \frac{5.0(2.90 - 1.65)}{10(1.65)} = 0.38 \text{ ppm}$$

Table 4

Analysis of Synthetic Water Samples

(Samples pre-concentrated 100 to 10 except as indicated)

Sample	Content ion	Taken ppm	Found ppm	Error ppm
A	Pb^{++}	0.25	0.26	+0.01
	Cd^{++}	0.12	0.12	±0.00
	Zn^{++}	0.05	0.06	+0.01
	Fe^{+++}	0.04	0.03	-0.01
A*	Pb^{++}	0.25	0.30	+0.05
	Cd^{++}	0.12	0.17	+0.05
	Zn^{++}	0.05	0.12	+0.07
	Fe^{+++}	0.04	0.05	+0.01
B	Pb^{++}	4.00	4.10	+0.10
	Cd^{++}	0.50	0.52	+0.02
	Zn^{++}	1.00	0.95	-0.05
	Fe^{+++}	1.00	0.90	-0.10
C	Pb^{++}	0.50	0.48	-0.02
	Cd^{++}	2.00	2.02	+0.02
	Zn^{++}	0.50	0.45	-0.05
	Fe^{+++}	0.20	0.25	+0.05
D	Pb^{++}	1.00	1.05	+0.05
	Cd^{++}	1.00	1.01	+0.01
	Zn^{++}	0.20	0.18	-0.02
	Fe^{+++}	1.50	1.40	-0.10
E*	Pb^{++}	1.50	1.55	+0.05
	Cd^{++}	0.75	0.70	-0.05
	Zn^{++}	0.25	0.36	+0.11
	Fe^{+++}	0.25	0.35	+0.10

*Without pre-concentration; sample mixed directly with standard water; Concentration factor F = 0.9.

Procedure, subsequently presented, was developed.

Sample Pre-Concentration.--Due to the rather low concentration levels of metallic ions in commonly found natural waters and technical considerations previously discussed, a sample pre-concentration procedure was developed. This procedure, modified from those employed by W. W. Ullmann, B. H. Pfeil, J. D. Porter and W. W. Sanderson [Anal. Chem. 34, 213-216 (1962)] and J. Crose (private communication, City of Bloomington Sewage Treatment Laboratory, Bloomington, Indiana). The procedure is simple, merely requiring the evaporation of the original sample from the initial volume (in this case 100 or 200 ml) down to about 8-9 ml, with the occasional careful addition of a few drops of nitric acid to help oxidize organic matter and prevent buildup of carbonate deposits on the wall of the concentration beaker. The sample, thus concentrated, is further prepared in appropriate fashion for polarographic measurement. With the Concentration Assembly shown in Figure 13, reduction in volume from 200 to 8 ml requires, on the average, about 45 minutes, while reduction from 100 to 8 ml may be accomplished in as little as 30 minutes.

ANALYTICAL PROCEDURE

The typical procedure for the analysis of a natural water sample with the instrument herein described is detailed in the following sub-sections. The procedure given is intentionally more lengthy and detailed than commonly necessary, so that all forseeable experimental possibilities may be accommodated. The procedure presented is that

used with the device as pictured in Figure 14; it consists of five parts: (A) Sampling, (B) Pre-Concentration, (c) Test Solution Preparation, (D) Instrument Operating Procedure, and (E) Calculation of Results.

(A) Sampling

The precise method of sampling must be determined by the analyst, based on the location of the body of water to be analyzed, the general nature of that body, and the specific application of the analytical results to be made.

Since sampling conditions and objectives vary widely, only the particular method employed in this study for sampling natural waters such as lakes, rivers, streams, pools, etc., is described. An Esmarch APHA-type Water Sampling Apparatus was used in all sample collecting. This apparatus permits one to collect a 200-ml sample at whatever convenient depth he chooses; a depth of 3 feet was selected for this study for no particular reason other than convenience in handling the sampling equipment, since the ability of the analyzer to function properly was under investigation, rather than the composition of the waters analyzed. The samples collected were either analyzed on location or transferred to clean, marked polyethylene bottles for transportation back to the laboratory, where analyses were performed at a convenient time.

(B) Pre-Concentration

1. Transfer the sample to be concentrated to the calibrated concentration beaker, filling the beaker just to the 200-ml mark (or

any other desired specific volume between 10 and 200 ml).

2. Assemble the apparatus as shown in Figures 13 and 14; add 2 or 3 'Boileezers' (Fisher Scientific Company) to the beaker to minimize bumping during evaporation.

3. Light the burner and adjust the gas control valve to permit steady operation of the burner.

4. Add 2 or 3 drops of nitric acid to the water sample, repeating this addition if noticeable buildup of solid material appears on the inside wall of the beaker during evaporation of the water.

5. Repeat the addition of 2 or 3 drops of nitric acid when the volume has been reduced to about 50 ml, then continue evaporating until the sample volume has been reduced to well under 10 ml, but do not evaporate the sample to dryness.

6. Turn the burner off and allow the sample to cool for at least 5 minutes. Then adjust the pH of the solution to a value between 5 and 7 by the dropwise addition of ammonia (test the pH with EM-Reagent indicator sticks) before proceeding to Test Solution Preparation.

(C) Test Solution Preparation

The standard addition procedure requires that one test solution which contains only the standard be measured, followed by a second solution measurement for the standard plus unknown. This study has indicated that it is advisable to make the measurement of the standard water once daily. The procedure for this measurement is identical to that outlined for the sample solution, except that distilled water, instead of the unknown sample solution, is added during the preparation of the test solution prior to mixing. The general procedure for standard

and unknown is as follows:

1. Transfer 1.0 ml of standard water to the 10-ml graduate (take care to properly pre-rinse the pipet).

2. If an unconcentrated sample is to be analyzed, simply add the unknown water to the graduate just to the 10-ml mark and proceed to step (C-4).

3. If a pre-concentrated sample is to be analyzed, carefully pour the concentrated sample from the concentration beaker into the graduate containing the standard water. Rinse down the inside wall of the beaker with a minimum quantity of distilled water, and transfer these washings to the graduate. Then add distilled water, if necessary, to bring the mixture just to the 10-ml mark.

4. Place a forefinger over the mouth of the graduate and quickly invert the graduate twice to mix sample and standard well.

5. Make sure that the instrument case cover brace (left side) is locked in the open position, then remove the cell vessel from its mounting clip, disengaging the nylon cover from the cell without removing the electrodes from the cover.

6. Half-fill the glass cell vessel with the Test Solution prepared in step C-4; immerse the electrodes in the solution in the cell and swirl the cell-electrode assembly momentarily to properly rinse all three electrodes and the gas bubbler; then discard the liquid in the cell.

7. Half-fill the cell again with the Test Solution remaining in the graduate. Replace the cell vessel in the mounting clip and position the electrode-cell-cover assembly in the cell.

8. Open the upper stopcock of the mercury reservoir and insert the platinum connecting wire (single black lead) through the stopcock opening as far as it will go.

9. Open the lower stopcock of the reservoir so that mercury begins to flow through the dropping mercury electrode capillary.

10. Carefully open the valve on the freon can and adjust it and the in-line stopcock connected with it until a flow of gas from the tip of the gas bubbler may be just barely felt on a moistened finger tip. Then, carefully insert the gas bubbler through the cell cover; readjust the can valve and/or line cock as needed to yield a flow rate through the test solution so that separate gas bubbles may be discerned. While the solution is being purged in this manner for at least 5 minutes, proceed to Instrument Operating Procedure, Preliminary Instrument Check or Test Solution Measurement, depending on the circumstances.

(D) Instrument Operating Procedure

Two series of operations should be completed prior to actual solution measurements. These are the Preliminary Instrument Check and the Slope Adjustment; each should be performed at least once daily (preferably just prior to the standard water measurement). The purpose of the first is to check the condition of the instrument batteries, while the second is necessary to compensate for residual current irregularities resulting from charging currents.

1. Preliminary Instrument Check.

   a. Open the battery compartment at the rear of the instrument

case and see that the electronic assembly multiple connector plug is properly connected with the battery pack receptacle and close the compartment.

b. With the Power Switch OFF, Compensate Control on 000, Function Switch on OFF, and Battery Switch on position 1, turn the Sensitivity Switch to position 2.

c. Turn the Power Switch ON and the Function Switch to position 1; the meter should read 0.8 or more (indicating a battery output of 8 volts). If the reading is less than 0.7, replace Batteries B_3 (4.05 volts each) and repeat the check.

d. Turn the Battery Switch to position 2--the meter should read 1.0 (full scale deflection); turn the Battery Switch to position 3--the meter should again read 1.0. If these two successive readings differ by more than 3 scale divisions or if either reading is less than 9.4 scale divisions, replace Batteries B_1 and B_2 (15 volts each).

e. Turn the Battery Switch to position 4. Adjust the Calibrate Control so that the meter reads exactly 1.00 (if this adjustment cannot be made, replace Batteries B_4 (1.35 volts each). DO NOT CHANGE this setting of the Calibrate Control during subsequent experimental measurements.

f. Return the Battery Switch to position 1 and the Function Switch to OFF; proceed to the Slope Adjustment.

2. Slope Adjustment.

a. When the 5-minute purging period has been completed, make

sure that the battery pack leads are connected via the connector plug, then raise the gas bubbler in the test cell so that a freon atmosphere is maintained over the solution in the cell without bubbling through the liquid.

b. Turn the Function Switch to position 1 and the Power Switch ON.

c. Adjust the Calibrate Control to yield a meter reading of exactly 0.35.

d. Turn the Function Switch to position 8 (variable potential) and depress the Protect Switch and Test Switch, in that order while carefully noting the meter reading.

e. Turn the Function Switch back to position 1 and readjust the Calibrate Control to a meter reading of exactly 0.45; again depress Protect and Test Switches in turn and note the meter reading.

f. If the meter reading in (e) is larger than that in (d), turn the Slope Control slightly clockwise; if smaller, turn the Slope Control slightly counterclockwise.

g. Repeat steps (b) through (f) until the meter readings are identical for steps (d) and (e). Take particular care not to change the Slope Control setting during subsequent instrument operations.

3. Test Solution Measurements.

a. Remove the cell lead plug from its storage clip in the instrument cover and connect the plug with its receptacle in the

upper left corner of the instrument panel.

b. When the 5-minute purging period has been completed, raise the gas bubbler in the test cell so that a freon atmosphere is maintained over the test solution.

c. Turn the Function Switch to position 2 and the Sensitivity Switch to position 2 (Position 1 represents 10 μA fullscale; position 2, 5 μA; position 3, 1 μA; and position 4, 0.5 μA). Check and see that the Compensate Control is at 000.

d. Depress the Protect Switch and while it is depressed, also depress the Test Switch, simultaneously rotating the Baseline Control to secure a meter reading of about 0.1 (5 scale divisions). Record this meter reading to the nearest 0.5 unit as the Baseline value 2. Release the Test Switch, then the Protect Switch, in that order.

e. Turn the Function Switch to position 3 (3 represents lead, 4 cadmium, 5 zinc, and 6 iron measurements).

f. Depress Protect and Test Switches simultaneously and record the maximum meter deflection after two successive needle swings are equal (usually after 3 to 5 swings); release Test and Protect switches. NOTE: In the event that the meter deflection exceeds the limits of the meter scale, the following procedure must be employed: (1) Adjust the Compensate Control until the meter deflection is on scale and maintain the setting of this control; (2) Reset the Function Switch to the setting used for the previous reading, i.e., if the offscale deflection occurred on 3, reset

the Function Switch to 2; if on 4, reset to 3, etc., then repeat the operations in (f) prior to NOTE. If this procedure fails to result in on-scale readings, the sample is too concentrated and another, more dilute, test solution must be prepared. (This eventuality is relatively unlikely, due to the range over which the Compensate Control is capable of operating.)

g. Repeat steps (e) and (f) respectively for Function Switch positions 4, 5, and 6 for successive measurement of cadmium, zinc, and iron waves.

h. Shutdown the instrument by turning Function Switch OFF, Power Switch OFF; disconnect the cell plug and replace it in its mounting clip. Remove the contact lead from the upper stopcock of the mercury reservoir and close both reservoir stopcocks. Empty the contents of the cell into the waste mercury container and rinse cell and electrodes with a small amount of distilled water prior to storage in the cell mounting clip.

4. Variable Potential Mode Operation (Recording Manual Polarograms).

a. With the Function Switch on position 1, set the Calibrate Control to the dial reading representing one-half the desired applied potential value, as read on the meter.

b. Turn the Function Switch to position 8 and record the indicated current from the meter.

c. Repeat steps (a) and (b) for each E vs. i point desired on the polarogram.

(E) Calculation of Results

Results are calculated with the standard addition formula:

$$C_x = \frac{C_x(i_{s+x} - i_s)}{F.i_s}$$

as shown in Table 3, where F is the concentration factor used. When two successive Function Switch position readings are the same, as for example: 3: 2.15, 4: 2.15, obviously, the ion whose wave height is represented by the reading at position 4 is either absent or is present in so small a concentration that it cannot be measured with the Model II analyzer.

RESULTS AND DISCUSSION

Analysis of Synthetic Samples.--A number of synthetic water samples containing various concentrations of Pb^{++}, Cd^{++}, Zn^{++}, and Fe^{+++} were prepared and analyzed by the procedures previously presented; the results of these analyses are shown in Table 4. Probably the most significant trends shown by these results are: (1) low concentrations of zinc and/or iron are quite likely to yield high results, and (2) lead and cadmium results are likely to be considerably more accurate than those for zinc and iron. These two conclusions are to be expected on consideration of the nature of the polarographic waves (Figure 15)--the sharp, well-defined nature of the lead and cadmium waves compared with the less distinct zinc and iron waves (even at higher concentrations than those shown in Figure 15) explains why the results for these latter ions are more likely to be erroneous. That the results for iron

may be high is to be expected since the iron wave is very close to the supporting electrolyte discharge wave. The pH of the system affects the location of this discharge wave rather dramatically, so that the 'rough' pH adjustment made at the end of the sample pre-concentration is rather important--the pH of the test solution must be between 5 and 7.

Analysis of Natural Waters.--A selection of various natural waters, largely collected from various 'sport-fishing' locations, was then analyzed, using the same method and procedure as employed with the synthetic samples. These results are shown in Table 5. Since no technique for independent analysis by other methods, such as atomic absorption spectroscopy, was available to the investigators, these results do not necessarily reflect accuracy, but do show the relative reproducibility of analyses of concentrated vs. unconcentrated samples. In the judgment of the investigators, the concentrated sample results are likely to be the more accurate for two principal reasons. First, at least some of the organic matter, likely to be present in a natural sample, which could complex a metallic ion and affect analysis adversely, is destroyed by nitric acid during pre-concentration. Secondly, inasmuch as the analyses of synthetic samples indicated a probable trend toward high results, the fact that the unconcentrated samples nearly always produced the higher results tends to support confidence in results following pre-concentration.

Critical evaluation of all the analytical results obtained,

Table 5

Analysis of Selected Natural Water Samples

(Samples pre-concentrated 200 to 10, except as noted)

No.	Source of Sample[a]	pH[b]	Metal Ion Concentrations Found			
			Pb^{++} ppm	Cd^{++} ppm	Zn^{++} ppm	Fe^{+++} ppm
1	Sport-fishing stream	6.0	N[c]	N	0.02	1.22
1[d]			N	N	N	1.48
2	Artificial impoundment	7.5	0.01	N	0.02	0.04
2[d]			N	N	N	0.06
3	Surface run-off	6.5	0.01	0.02	N	0.30
3[d]			N	0.02	N	0.06
4	'Polluted' creek	5.5	0.02	N	0.15	1.35
4[d]			N	N	0.08	1.70
5	'Great' lake	7.5	N	N	0.24	0.08
5[d]			N	N	0.32	0.11
6	'Large' river	6.5	0.03	N	0.09	0.62
6[d]			0.02	N	0.15	0.70
7	Farm well	7.0	N	0.02	0.28	0.18
7[d]			N	0.01	0.20	0.26
8	Strip-mine pit	3.5	0.05	0.01	0.75	2.44
8[d]			0.07	0.01	0.60	2.86
9	Industrial effluent	6.5	0.78	0.42	0.45	0.56
9[d]			0.80	0.38	0.54	0.70
10	Mine drainage slough	5.0	1.40	0.32	3.42	0.25
10[d]			1.44	0.30	3.65	0.20

[a] Samples collected at average depth of 3 feet under surface of water, using Esmarch APHA-type Water Sampling Apparatus.

[b] pH estimated with EM-Reagents Non-Bleeding pH Indicator Sticks to nearest 0.5 pH unit; Series 5-10 pH and 0-6 pH used.

[c] Table entry 'N' indicates that the metal was not measurable with the apparatus and technique used.

[d] Samples analyzed without pre-concentration.

including a substantial number not tabulated herein, leads the investigators to estimate the 'Instrument Reliability' figures shown in Table 6. These figures are quite conservative, allowing for a safety factor of perhaps 2, since comparison of analytical results with other methods was not actually accomplished. However, the authors feel that these figures are realistic for predicting the nature of the results one might expect from the Model II analyzer and the method presented here.

Comparison of the 'Instrument Reliability' estimates with toxic limits for fish and permissible concentrations for water supplies, as shown in Table 6, indicates that the analyzer is applicable for measurements of critical values for these ions in most waters. It is also worth pointing out that the level of biological and/or organic pollution expected in so-called sporting waters--the type of waters for which the analyzer was designed--is quite likely to be much less than in waters 'closer to civilization.' The point, then, is that the comparison of the instrument's performance with the toxic limits for fish (the more favorable comparison) is quite promising.

Advantages and Disadvantages of the Model II Analyzer.--Among the advantages of the Model II analyzer are the following: (1) the device is readily portable, weighing only about 15 pounds; (2) it is capable of yielding analytical results, in the field, for some metal ions which are relatively difficult to determine otherwise under similar conditions; (3) it is relatively easy to operate; (4) the chemical operations required are extremely simple; (5) it is designed for relatively simple maintenance, requiring only occasional replacement of

Table 6

Comparison of Metal Ion Toxic Limits with Instrument Reliability[a]

Metal Ion	Toxic Limit[a] ppm	Permissible Concentration[b] ppm	Instrument Reliability[c] Without pre-concn ppm	Instrument Reliability[c] With pre-concn ppm
Pb^{++}	0.1	0.05	±0.05	±0.03
Cd^{++}	0.5	0.01	±0.05	±0.03
Zn^{++}	1	5	±0.1	±0.05
Fe^{+++}	0.9	0.3	±0.4	±0.2

[a]Toxicity of dissolved metals to fish, according to C. C. Van Duijn, "Diseases of Fishes", 2d Ed., C. C. Thomas Publishers, Springfield, Illinois, 1967.

[b]Permissible trace element concentration in surface waters for public water supplies, from J. F. Kopp and R. D. Kroner, "Trace Metals in Waters of the United States", U. S. Department of the Interior, Federal Pollution Control Administration, Cincinnati, Ohio, 1967.

[c]Estimates of principal investigator, based on experimental measurements with known samples under varying conditions, for a metallic ion concentration range of 0.2 to 5 ppm in each case.

propane (each 6-ounce can may concentrate 6 to 10 samples), Freon-12 (each 15-ounce can is sufficient for 20-30 analyses), and batteries (lifetime is widely variable); (6) the cost of the total instrument (under $100) is quite minimal in comparison with other currently available equipment; (7) the variable potential mode incorporated in the analyzer permits the exploration, with the instrument, of the possibilities for adapting the device to the use of other electrolyte systems and/or other metallic ions; and (8) the presence of two unused Function Switch positions (7 and 9) and additional trimpots in the ramp supply circuit (Figure 2) also contribute to future development and adaptation to other analyses.

Disadvantages of the device include: (1) it is limited, at present, to the determination of only four metallic ions; (2) the operating procedure and calculations, although relatively simple by practicing chemists' standards, may appear to be quite complex to the novice; (3) the use of a mercury electrode makes proper disposal of waste materials after analysis important; (4) the life-time of the Type K10 15-volt batteries is relatively limited, and these should be replaced with a larger, higher capacity variety; (5) comparison of the results attainable with the device and the results from completely different reliable methods (such as atomic absorption spectroscopy) is not now available, so that accuracy of analysis of natural samples is still a matter for some conjecture.

CONCLUSIONS

Although not all the original objectives of the project were realized, the main goal was reached--the development of a field device for determination of (certain) heavy metals in natural waters. A number of relatively unique and interesting techniques were developed for the analyzer, such as the sample concentration assembly, the use of freon for oxygen purging, the DME reservoir system, and perhaps some of the concepts involved in electrical circuitry.

The device has been designed so that others may extend and/or improve its performance and applications. Unfortunately, the author's commitments are such that he is unlikely to be able to do so.

Perhaps one of the most important contributions of this project to present-day science is that a rather large number of people--scientists, non-scientists, and pseudo-scientists--became more interested in the environmental water problems surrounding us while observing the instrument under construction, hearing us talk about it and our problems in its design and development, or while watching our rather unorthodox operations during field tests in all sorts of unlikely locations for analytical chemists!

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September 30, 1970

Robert E. Van Atta
Principal Investigator